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"Crystal Growth in Substrate-Confined Liquids"

TECHNICAL REPORT

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SUMMARY

The task objective ^{was} is to develop crystal growth techniques utilizing substrate-confined-liquids (S.C.L.). In particular, crystals ^{were} ~~will~~ usually be grown as *arrays* of single crystals and ^{included} ~~will include~~ semiconductors useful as detectors.

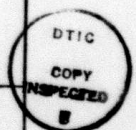
The primary technical problem remaining at this time ^{was} ~~is~~ to extend techniques for growing a single crystal at each location in the array to include semiconductors useful in photodetection.

The basic approach ^{was} ~~is~~ experimental, utilizing a laboratory already equipped for vacuum evaporation and C.V.D. with analysis largely by optical, x-ray, and SEM techniques.

The main result obtained so far ^{was} ~~is~~ that arrays of In single crystals *PARALLEL TO* can be grown with a common basal plane orientation: (101) ^{exhibited} ~~||~~ substrate surface. These crystals exhibit facets on their upper surfaces closely parallel to the substrate surface. Also cleaning procedures were developed for the In, which should be useful for In compounds as well.

The main importance of this result is the possibility of carrying it over to the useful detector materials, InSb and CdTe. Based on various earlier findings, there appears to be a fair probability that stoichiometric growth of such semiconductors should occur similarly to that of In noted above.

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DETAILED REPORT

The last technical report described several experiments to grow arrays of crystals in suitably shaped surfaces of inert substrates. While those experiments were only partially successful, they suggested two main possibilities for further work: (1) solution growth, as in the Ge-Au system studied there, and (2) stoichiometric growth in systems exhibiting not too large a contact angle ($\theta \lesssim 135^\circ$). In addition, several improvements in experimental techniques were suggested, which have since been adopted.

Stoichiometric growth appears the easier of the two suggested approaches, based on our experience to date with elements. Germanium has been grown and, as was noted in the last report, readily grows crystals larger than the concavity, or pit, size used in our substrates. However, no preferred orientation was observed in that Ge work and liquid stability in the concavities was tenuous due to the large contact angle, $\theta \gtrsim 150^\circ$.

In the present work period, we have done many experiments with In, which has a favorable contact angle near 90° and typically grows crystals of $\gtrsim 50 \mu\text{m}$ size. The longer-term purpose in working with In (and Te, as will be mentioned) is in preparation to grow In compounds (and CdTe). Even with a favorable case like In, however, difficulties had to be overcome. Cleaning of In in 800°C H_2 , for example, was observed to be insufficient, as judged by droplet shapes on the substrate field, and the addition of a preliminary wet H_2 step was therefore introduced. With this two-step procedure, the droplet behavior becomes textbook - ideal and during freezing a facet, rather accurately parallel to substrate surface and quite flat, develops on the In droplet in each concavity.

Diffraction measurements on several substrates with a variety of differently

shaped concavities show only the In (101) and (202) reflections[†], and these reflections appear at the right θ values for the (101) plane parallel to the substrate surface. FWHM for peaks is about 0.2° in the 2θ plot, even through the x-ray beam was incident on an array of some 10,000 crystals. Sensitivity was such that if a second orientation parallel to substrate was present at 1/10 strength of the (101) it would have been easily detected. No such second orientation was observed. It appears, therefore, that (101) plane grows parallel to substrate surface and is the plane exhibiting the facet at the top of each crystal.

Laue patterns were made for a variety of concavity shapes and with several accelerating voltages applied to the Mo target tube, down to 10 keV. The lower voltages were used to favor the overlying layer of In, typically 5 μm thick, over the underlying Si. Only the Si Laue pattern could be observed, however, so that there does not appear to be any azimuthal orientation in the In (101) platelet crystals in the concavities.

These results do not follow simply from models currently being considered. Graphoepitaxy would predict a definite azimuthal orientation, for example, from nucleation events at the interior corners of a concavity. Diatoxy proposals probably are best tested for a crystal that floats in its melt, which is not the case for In, so no simple prediction can be made for In.

Similar experiments are underway with Te, the main purpose being in preparation for growth of CdTe. Some rather striking faceting has been observed in the optical microscope, but more controlled preparations will be needed before these can be correlated with other parameters of the experiments.

Turning now to solution growth, we were eager to follow up on the encouraging

[†] referred to the b.c. tetragonal unit cell. FCC approximate equivalent is (111).

observation noted in the last report, of growth of a single Ge crystal in many of the concavities containing Au-Ge solution*. Some experiments were performed with germane passed over In-containing concavities. However, the C.V.D. set up used for the experiments had previously been used for HgCdTe among other things and introduced contaminants. It is presently being extensively cleaned for another try. Other experiments were performed in a freshly cleaned hydrogen furnace, introducing Sb into an array of In droplets. These experiments were roughly similar to the Ge-Au experiments, including cooling rates of $\sim 1^\circ/\text{minute}$, but in the present case led to rather complex growths, probably involving constitutional supercooling. Due to the complexities exhibited in those growths and due to the limited time remaining on the contract, we will be pursuing the InSb work only with stoichiometric compositions. With some modifications of quartzware (and the addition of a means to sense recalescence heat) the stoichiometric growth conditions will be studied.

* in that system, a eutectic growth appears in addition to the single crystal noted.